Complexes of Bis(thiophene 2-carboxaldehyde)-o-tolidin with Transition Metal Ions

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Received 11 December 1982; revised and accepted 25 August 1983

Complexes of bis(thiophene 2-carboxaldehyde)-o-tolidin (o-tolidin = 4,4'-diamino-3,3'-dimethylbiphenyl) with Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Ru(III), Pd(II), Ir(IV), Pt(IV) and Au(III) have been prepared. The complexes have been characterised on the basis of analytical, conductance, IR spectral, electronic spectral and magnetic moment data. IR spectra show that the ligand acts as a tetradentate molecule. Molar conductance data in DMF indicate that Rh(III) and Ir(IV) complexes are non-electrolytes; Co(II), Cu(II), Ru(III) and Au(III) are 1:1 electrolytes; Mn(II), Fe(III), Ni(II) and Pd(II) complexes are 1:2 electrolytes; and Pt(IV) complex is 1:4 electrolyte. The ESR spectrum of Cu(II) complex shows a compressed rhombic symmetry with a distorted trigonal-bipyramidal geometry probably with $d_{2}$ ground state. The magnetic moments of the complexes show that all the complexes except Co(II) complex are of high-spin type. The Co(II) complex shows a spin paired-spin free equilibrium.

Materials and Methods

Chlorides of Mn(II), Co(II), Cu(II), Ni(II) and Fe(III) were BDH reagents of AR grade while RuCl$_3$, RhCl$_3$, Na$_2$PdCl$_4$, Na$_2$IrCl$_6$, Na$_2$PtCl$_6$ and AuCl$_3$ were J. and M. (U.K.) products. These were used as such for the preparation of the complexes.

The ligand bis(thiophene 2-carboxaldehyde)-o-tolidin was prepared by refluxing o-tolidin (4,4'-diamino-3,3'-dimethylbiphenyl) (1 mol) with thiophene 2-carboxaldehyde (2 mol) in benzene for 3 hr, allowing the mixture to cool down and separating the solid by filtration. The crude product thus obtained was recrystallised from benzene (m.p. 183°C).

The complexes were prepared by mixing the solutions of metal salts in ethanol with the ligand dissolved in minimum amount of benzene in the molar ratio of 1:1. The mixture was stirred for 2-4 hr. The precipitate thus obtained was filtered and washed with hot ethanol and then with hot benzene and dried over anhydrous CaCl$_2$ in vacuo.

The complexes were analysed for C, H and N by the microanalytical methods. The molar conductances of the complexes at 10$^{-3} M$ dilution in dimethylformamide were measured using a Philips conductivity bridge model PR-9500 with a dip-type conductivity cell. The magnetic measurements were made on a Gouy balance at room temperature and diamagnetic corrections were applied. The reflectance spectra of the complexes were recorded at G.N.D. University, Amritsar. The IR spectra were recorded in KBr phase in the range of 4000-200 cm$^{-1}$ on a Perkin Elmer 621 infrared spectrometer. The thermogravimetric analyses and differential thermal analyses of the complexes were done at RRL, Hyderabad and the ESR spectra of the complexes were recorded at IIT, Madras on an X-band spectrometer.

Results and Discussion

The elemental analyses (Table 1) for C, H and N show that bis(thiophene 2-carboxaldehyde)-o-tolidin forms complexes with Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Ru(III), Rh(III), Pd(II), Ir(IV) and Au(III) in the molar ratio of 1:1. The molar conductances in DMF indicate that the complexes of Rh(III) and Ir(IV) are non-electrolytes, the complexes of Co(II), Cu(II), Ru(III) and Pd(II) are 1:2 electrolytes except the Pt(IV) complex which is 1:4 electrolyte (Table 1). Mn(II) and Au(III) complexes seem to undergo solvolysis in dimethylformamide.

In the ligand, bis(thiophene 2-carboxaldehyde)-o-tolidin the νC=N appears at 1610 (vs) and the νC=S at 7008 cm$^{-1}$. Bellamy$^{7}$ reports νC=S absorption at 600-700 cm$^{-1}$. On complexation νC=N shows a large positive shift of up to 40 cm$^{-1}$. The ring vibrations
show marked down field shifts showing thereby that azomethine nitrogen and heterocyclic sulphurs take part in coordination. Thus, the ligand molecule acts in a tetradenate manner. On the basis of the IR data and conductivity data it can be said that the complexes of Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Ru(III), Rh(III), Pd(II), Ir(IV), Pt(IV), and Au(III) are 4, 5, 5, 4, 5, 6, 7, 4, 8, 4 and 6 coordinate respectively. The results are further supported by the far IR spectra of complexes which show three bands in the region 425-400, 345-310 and 295-270 cm⁻¹ which have been assigned to M-N, M-S and M-Cl vibrations.

The thermograms (TGA and DTA) of rhodium, platinum and palladium complexes were recorded. They show similar features of decomposition in all these complexes. The order of heat stabilities is: Rh > Pd > Pt.

**Reflectance spectra magnetic moments**

The reflectance spectrum of Mn(II) complex of bis(thiophene 2-carboxaldehyde)-o-tolidin shows bands which have high intensities and the spectrum is comparable with that of [Mn Br₄]²⁻ indicating tetrahedral geometry of the complex. In addition to d-d bands in the spectra, there are two charge-transfer bands at 40,000 and 3330 cm⁻¹. The Fe(III) complex of bis(thiophene 2-carboxaldehyde)-o-tolidin shows bands at 37737, 34483, 31745 and 27777 cm⁻¹ in its reflectance spectrum. The bands have been assigned to charge transfer. The other bands at 22325 and 20,000 cm⁻¹, which have shoulders at 24390 and 18118 cm⁻¹ respectively, seem to be d-d bands characteristic of coordination number five in Fe(III). Since both the bands split into two, it has been assumed that this complex is highly distorted.

The molar conductivity of the Co(II) complex of bis(thiophene 2-carboxaldehyde)-o-tolidin suggests that the complex should be five coordinated. Its spectrum shows bands at 28571, 17391, 16393 and 9900 cm⁻¹. These bands neither fit the assignment of octahedral structure nor of any of the five coordinate structures. Probably the complex is so much distorted as to have a geometry in between trigonal bipyramidal and square pyramidal.

The Ni(II) complex of bis(thiophene 2-carboxaldehyde)-o-tolidin shows bands at 26667, 16000, 8163 and 3500 cm⁻¹ which have been assigned to tetrahedral stereochemistry. Cu(II) complex of bis(thiophene 2-carboxaldehyde)-o-tolidin shows bands at 30769, 18180, 16667 and 10417 cm⁻¹. The first intense band is of charge-transfer type, and the remaining three are d-d bands which indicate five coordinate structure; the bands have been assigned to dₓz−dₓz, dₓz−dₓz and dₓz−dₓz transitions respectively. The dₓz ground state has been confirmed by ESR spectrum of the complex.

The spectrum of Ru(III) complex with bis(thiophene 2-carboxaldehyde)-o-tolidin shows two charge-transfer bands at 40,000 and 37037 cm⁻¹ and a number of d-d bands at 29410, 25640, 16950, 14600 and 12820 cm⁻¹, which have shoulders at 24390 and 18118 cm⁻¹ respectively, seem to be d-d bands characteristic of coordination number five in Fe(III). Since both the bands split into two, it has been assumed that this complex is highly distorted.

The molar conductivity of the Co(II) complex of bis(thiophene 2-carboxaldehyde)-o-tolidin suggests that the complex should be five coordinated. Its spectrum shows bands at 28571, 17391, 16393 and 9900 cm⁻¹. These bands neither fit the assignment of octahedral structure nor of any of the five coordinate structures. Probably the complex is so much distorted as to have a geometry in between trigonal bipyramidal and square pyramidal.
cm\(^{-1}\) characteristic of octahedral environment\(^{15}\) around Ru(III) in this complex.

The spectrum of the Rh(III) complex of bis(thiophene 2-carboxaldehyde)-o-tolidin shows bands which do not tally with the previous assignments for six coordinate geometry. There are a number of additional bands besides those expected for a six coordinate complex. Thus, these bands have not been assigned with certainty.

The reflectance spectrum of Pd(II) complex of bis(thiophene 2-carboxaldehyde)-o-tolidin shows a square-planar environment around the palladium ion. Bands at 39215 and 35175 cm\(^{-1}\) have been assigned to charge-transfer transitions and bands respectively.

Bands at 29410, 25640, 24390, 20830, 18510, 17000, 15505 and 35085 and 33330 cm\(^{-1}\) correspond to the values expected for high-spin complexes and thus match with all the previous reports. The magnetic moment of cobalt(II) which is 3.82 B.M.\(^{18,20}\); values in the range 3.44-3.51 B.M. for cobalt(II) complexes of a macrocyclic 30-membered schiff base ligand have also been reported.\(^{19}\) The low value of the magnetic moment may be due to the presence of spin paired-spin free equilibrium in the complex.

Electron spin resonance spectra

The ESR spectrum of the copper(II) complex of bis(thiophene 2-carboxaldehyde)-o-tolidin was recorded at liquid nitrogen temperature (LNT). The spectrum is characteristic of rhombic symmetry with two g values, \(g_1 = 2.108\) and \(g_2 = 1.9791\), thus giving the value of \(g\) (average) = 2.065. The value of lowest \(g\) is less than 2.04, which indicates a compressed rhombic structure with distorted trigonal-bipyramidal stereochemistry. Again the shape of the spectrum indicates the presence of exchange coupling and the value of \(g\) (nearly equal to 2), indicates the \(d_{xy}\) ground state.\(^{16}\)

When the spectrum of the frozen solution of this complex was recorded at LNT in pyridine, \(<g> = 2.067\), it showed hyperfine structure (4 lines) due to the interaction with nuclear spin (\(^{63}\)Cu) and further the \(A_1\) component of the band showed superhyperfine splitting into seven peaks due to interaction with the nuclear spin of nitrogen \((I_N = 1)\). The \(<A_1> = 170\) G and \(<A_N> = 20\) G. The seven hyperfine lines can be the result of the interaction of three nitrogens simultaneously with a single molecule. But it is very difficult to assess whether three nitrogens are all of pyridine solvent or any nitrogen of the ligand is also involved.

The spectrum of the complex was also recorded in DMSO frozen solution, \(<g> = 2.081\). In this spectrum the hyperfine splitting due to nucleus was observed and \(<A_1> = 115\) G, but here no superhyperfine structure could be observed. In this case \(A_1\) component of the spectrum was much raised. It is, therefore, concluded that the solvent pyridine causes superhyperfine splitting.

References